§19. First-Principle (Ab Initio) Molecular Dynamics Simulations of Proton Transfer Phenomenon in Ion Liquid

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Liquids that consist of polar molecules including water are known to have high electrical conductivity due to rapid proton motion among molecules inside them. Organic ion liquid (molten salt) which has a melting point typically between room temperature and 100C, and is versatile at atmospheric pressure, shows by an order of magnitude even higher electrical conductivity than water. The ion liquids are currently under intensive and extensive research of energy-related and environmental-safe materials.

Imidazole is white powder at room temperature, becomes liquid around 80C. It consists of a $C_3N_2H_5$ 5-membered ring (molecular weight 69) as depicted in Fig.1. This is a polar molecule because of the asymmetry where one of two nitrogen atoms in the ring lacks a hydrogen atom, and protons are believed to hop quickly among these molecules using this asymmetry (so-called Grotthus mechanism) to yield anomalously high electrical conductivity.

We have started studying this phenomenon for the imidazole liquid by means of quantum mechanical simulation technique which is based on the density functional theory of electrons. This method is usually called the first-principle molecular dynamics (MD) simulation of the Car-Parrinello type [1,2].

As the simulation domain, a rectangular box containing 16 imidazole molecules is taken where a group of four molecules of specific orientations constitute a basis set due to polarity. In order to find the optimized configuration (initial condition) for the subsequent MD run, these molecules need to be first energy minimized under the quantum mechanical forces, where the conjugate move

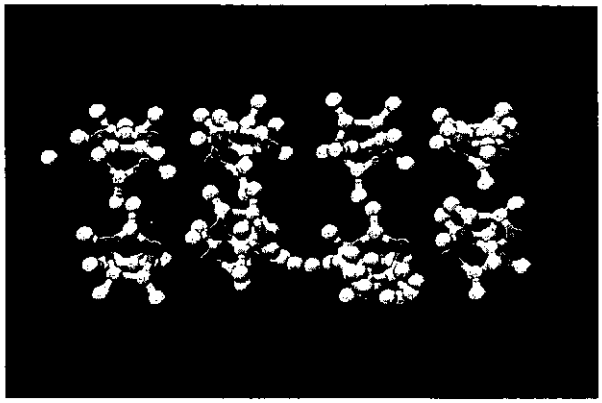

Fig.1 Trace of a proton moving among imidazole 5-membered ring molecules (every 5fs) in the first-principle molecular dynamics simulation.

is used in the Siesta run. The adopted time step is 1fs, and it takes a few ps before the positions are optimized. Then, a MD run is started under the constraint of constant temperature 400K, as is typical for the substance in real life. For this purpose, a reservoir known as the Nose-Hoover thermostat is used.

Figure 1 shows the trace of a proton moving in imidazole liquid in every 5fs [3], where the proton starts from an intermolecular vacuum space on the left side, moves rightward, and is encircling around one of the molecules. This reveals that the proton motion is highly influenced by quantum mechanical (atomic) forces from molecules. Further runs are now undertaken to investigate the proton transfer in imidazole ion liquid.

[1] R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2371(1985)

[2] A. Garcia et al., Siesta (Spanish initiative for electronic simulations with thousands of atoms), http://www.uam.es/departamentos/ciencias/siesta/

[3] Y.Zempo and M.Tanaka, NIFS Newsletter, February/March (2004) [in Japanese].